

Europäisches
PatentamtEuropean
Patent OfficeOffice européen
des brevets

REC'D 16 APR 2004	
WIPO	PCT

REC'D 16 APR 2004	
WIPO	PCT

Bescheinigung

Certificate

Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

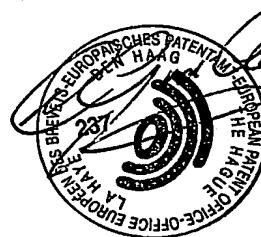
Patentanmeldung Nr. Patent application No. Demande de brevet n°

03252063.7

**PRIORITY
DOCUMENT**
SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

Der Präsident des Europäischen Patentamts;
im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

C. v.d. Aa-Jansen

BEST AVAILABLE COPY



Anmeldung Nr:
Application no.: 03252063.7
Demande no:

Anmeldetag:
Date of filing: 01.04.03
Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

UNILEVER PLC
Unilever House,
Blackfriars
London EC4P 4BQ
GRANDE BRETAGNE

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se referer à la description.)

Personal care compositions

In Anspruch genommene Priorität(en) / Priority(ies) claimed /Priorité(s) revendiquée(s)
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/
Classification internationale des brevets:

A61K7/00

Am Anmeldetag benannte Vertragstaaten/Contracting states designated at date of filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LU MC NL
PT SE SI SK TR LI

PERSONAL CARE COMPOSITIONS

Field of the Invention

5

The present invention relates to hair care compositions comprising polymers, and to their use in the treatment of hair.

10 Background and Prior Art

Hair styling sprays, mousses, gels, shampoos and conditioners frequently contain resins, gums and adhesive polymers to provide a variety of benefits, for example, 15 film-forming ability, thickening, sensory properties and hair shaping and setting.

It is known that compositions containing certain known hair styling polymers can perform poorly under conditions of high 20 humidity. Thus, hair styled with these compositions can lose its shape and any other benefits conferred by the compositions when the ambient humidity increases or the hair and/or the scalp becomes damp.

25 Furthermore there are many sensory negatives associated with conventional polymers as they have tendency to give a sticky feel when applied to the hair, they can make the hair feel stiff and they can leave deposits.

30 Polymers for use in cosmetic and personal care compositions, such as for styling hair, are usually linear or graft homo-

or co-polymers which contain various monomers in an alternating, random manner.

5 The hydrophobic/hydrophilic character of modern styling resins is carefully balanced to produce materials that are soluble in hydroalcoholic solvents, typically 80% VOC (volatile organics content).

10 Block copolymers have an advantage over conventional polymers in that the polymer architecture can be controlled more readily. This is particularly important when designing polymers with segments of distinct physical and chemical properties for particular applications. WO 98/53794 discusses $(AB)_n$ block copolymers, where A is a silicone block and B is a vinylic block. US 5,271,930 (Fintex Inc) 15 describes benzoate esters of polyalkoxylated block copolymers, such as PLURONICS™, for skin and hair care compositions. US 5,472,686 and US 5,660,819 (both Nippon Unicar) describe non-hydrolysing block copolymers comprising 20 a linear polysiloxane-polyoxyalkylene block as a repeating unit in cosmetic formulations. US 5,965,115 and US 5,972,356 (both Procter & Gamble) describe the use of 25 silicone-polyoxyalkylene copolymer surfactants for improving stability of a polyorganosilicone emulsion in personal care compositions.

It is an object of the present invention to provide polymers which may be used in cosmetic and personal care compositions, such as hair styling compositions, which 30 exhibit advantages over the compositions of the prior art. In particular, the invention aims to provide a class of

polymers for use in hair styling compositions. It is a further aim of the present invention to provide cosmetic and personal care compositions (e.g., hair styling compositions) which have relatively good solubility properties (eg, in 5 water, an alcohol such as ethanol or another cosmetically acceptable solvent) and perform surprisingly well under conditions of high humidity without the sensory negatives mentioned above.

10 **Summary of the Invention**

In a first aspect, the present invention provides a personal care composition comprising a polymer comprising an ABA block copolymer, wherein the A groups are polymeric blocks 15 built up from an ethylenically unsaturated polymerisable monomer and the B group is derived from an ethylenically unsaturated carboxylate together with a cosmetically acceptable diluent or carrier.

20 In another aspect, the present invention provides a cosmetic method of treating hair which comprises applying to the hair a composition according to the invention.

A further aspect of the invention is the use of a 25 composition of the invention for the cosmetic treatment of hair.

Detailed Description of the Invention

ABA Block Copolymers

5

The polymers of the invention may simply be ABA block copolymers or they may comprise the ABA block copolymers, with further modification such as, for example, by grafting onto the ABA block copolymer or by further reaction of the 10 ABA block copolymer.

The polymers of the invention are preferably soluble in a solvent selected from water, ethanol and mixtures thereof. Typically, the polymers are soluble in these solvents at a 15 level of at least 1% by weight, more preferably at least 5% by weight, most preferably at least 10 % by weight, at 25°C.

A blocks may be bonded directly to B blocks, where the chemistry of the A and B blocks permits this.

20 Alternatively, the A blocks may be bonded to the B blocks via a suitable linker group L, so that the ABA block copolymer is of the formula A-L-B-L-A or, where the B block is branched or hyper branched, B(-L-A)_n. Polymers of formula A-L-B-L-A and B(-L-A)_n fall within the meaning of the term 25 ABA block copolymer, as used herein. Typically, L is a divalent group having a molecular weight of from 14 to 200 Daltons which links the A and B blocks, preferably via O-C, N-C or S-C bonds to the B block. Preferably L is selected from:

-R-C(O)-O-;

-R-O-C(O)-O- ;

5 -R-C(O)-N(R')- ;

-R-O-C(O)-N(R')- ; or

-R-N(R')-C(O)-N(R'')- ;

10

in which R is a divalent, optionally substituted, linear or branched C₁-C₁₈ hydrocarbon radical (such as C₁-C₁₂ alkylene), and

15 R' and R'' are independently selected from monovalent, optionally substituted, linear or branched C₁₋₁₈ hydrocarbon radicals e.g., C₁-C₁₈ alkyl, such as methyl.

20 Preferably, the divalent linker group is a carbonylalkylene group containing from 2 to 7 carbon atoms which forms an ester linkage to the B block, such as, for example, a group of formula -C(O)-C(CH₃)₂-.

25 Examples of monovalent, unsubstituted radicals are alkyl radicals, such as the methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, n-pentyl, iso-pentyl, neo-pentyl and tert-pentyl radical; alkoxy radicals, such as the methoxy, ethoxy, n-propoxy, iso-propoxy, n-butoxy, iso-butoxy, tert-butoxy, n-pentoxyl, iso-pentoxyl, neo-pentoxyl and 30 tert-pentoxyl radicals; hexyl radicals, such as the n-hexyl radical; alkenyl radicals, such as the vinyl, allyl, 5-

- 6 -

hexenyl, 4-vinylcyclohexyl and the 3-norbornenyl radical; cycloalkyl radicals, such as cyclopentyl, cyclohexyl, 4-ethylcyclohexyl and cycloheptyl radical; norbornyl radicals and methylcyclohexyl radicals; aryl radicals, such as the phenyl, biphenylyl, napthyl, anthryl and phenanthryl radical; alkaryl radicals, such as o-, m- and p-tolyl radical, xylyl radicals and ethylphenyl radical; and aralkyl radicals, such as the benzyl, styryl, and phenylethyl radicals.

10

Examples of monovalent, substituted radicals are halogenated hydrocarbon radicals, such as the chloromethyl, 3-chloropropyl, 3-bromopropyl, 3,3,3-trifluoropropyl and 5,5,5,4,4,3,3-heptafluoropentyl radical and the chlorophenyl, dichlorophenyl and trifluorotolyl radical; mercaptoalkyl radicals, such as the 2-mercptoethyl and 3-mercaptopropyl radical; cyanoalkyl radicals, such as the 2-cyanoethyl and 3-cyanopropyl radical; aminoalkyl radicals, such as the 3-aminopropyl, N-(2-aminoethyl)-3-aminopropyl and N-(2-aminoethyl)-3-amino-(2-methyl)propyl radical; aminoaryl radicals, such as the aminophenyl radical; acyloxyalkyl radicals, such as the 3-acryloxypropyl and 3-methacryloxypropyl radical; and hydroxyalkyl radicals, such as the hydroxypropyl radical.

25

Preferred monovalent radicals are independently selected from unsubstituted or substituted C₁ to C₆ alkyl radicals or optionally-substituted-phenyl radicals, in particular, methyl, ethyl, propyl or phenyl radicals.

30

Examples of divalent hydrocarbon radicals are linear or branched saturated alkylene radicals, such as the methylene and ethylene radical, as well as propylene, butylene, pentylene, hexylene, cyclohexylene and octadecylene

5 radicals; alkoxyalkylene radicals such as the methoxyethylene and ethoxyethylene radical; unsaturated alkylene or arylene radicals, such as the hexenylene radical and phenylene radicals; alkarylene radicals such as the methylphenylene and ethylphenylene radical, and

10 alkoxyarylene radicals such as the methoxyphenylene and ethoxyphenylene radical. The divalent hydrocarbon radical R can be interrupted by divalent radicals, bonded to carbon atoms on both sides, such as -O-, -C(O)O-, -O(O)C-, -CONR⁶-, -NR⁶C(O)- and -C(O)-, where R⁶ is hydrogen or a monovalent,

15 optionally substituted, linear or branched C₁₋₁₈ hydrocarbon radical as described above.

It is preferable if in the molecular weight M_n of the total polymer is from 1,000 to 1,000,000, more preferably 5,000 to

20 500,000.

The A Blocks

The A blocks in the copolymers of the invention are of a

25 polymer that is derived from an ethylenically unsaturated polymerisable monomer.

By "polymerisable" is meant monomers that can be polymerised by reaction between the monomers to form an extended polymer

30 chain which is typically linear.

By "ethylenically unsaturated" is meant monomers that contain at least one polymerisable carbon-carbon double bond (which can be mono-, di-, tri- or tetra-substituted).

5 Either a single monomer or a combination of two or more monomers can be utilised. In either case, the monomers are selected to meet the physical and chemical requirements of the final ABA block copolymer.

10 The A blocks, which may be the same or different in each ABA block copolymer (but which are preferably the same) preferably have a molecular weight M_n in the range of from 100 to 200,000 more preferably from 1,000 to 100,000, most preferably 1,000 to 20,000.

15 Suitable ethylenically unsaturated monomers include those having the following general formula:



20 in which R^{11} and R^{12} are independently selected from hydrogen, C_1-C_{10} straight or branched chain alkyl, methoxy, ethoxy, 2-hydroxyethoxy, 2-methoxyethyl and 2-ethoxyethyl groups;

25 G is selected from hydroxyl, $-O(M)_{2/v}$, $-OR^{13}$, $-NH_2$, $-NHR^{13}$ and $-N(R^{13})(R^{14})$;

-----where M is a counter-ion of valency v selected from metal ions such as alkali metal ions and alkaline earth metal ions, ammonium ions and substituted ammonium ions such as 30 mono-, di-, tri- and tetraalkylammonium ions, and each R^{13}

and R¹⁴ is independently selected from hydrogen, C₁-C₄₀ straight or branched chain alkyl, optionally substituted with one or more groups selected from hydroxy, amino, C₁-C₃ alkoxy, C₁-C₃ alkylamino and di(C₁-C₃ alkyl)amino, for example

- 5 N,N-dimethylaminoethyl, 2-hydroxyethyl, 2-methoxyethyl, and 2-ethoxyethyl. Representative non-limiting examples of monomers useful herein include protected or non-protected acrylic acid and methacrylic acid and salts, esters and amides thereof.

10

The salts can be derived from any of the common nontoxic metal, ammonium, or substituted ammonium counter ions. The esters can be derived from C₁₋₄₀ straight chain, C₃₋₄₀ branched chain, or C₃₋₄₀ carbocyclic alcohols, from polyhydric alcohols

- 15 having from about 2 to about 8 carbon atoms and from about 2 to about 8 hydroxyl groups (non-limiting examples of which include ethylene glycol, propylene glycol, butylene glycol, hexylene glycol, glycerol, and 1,2,6-hexanetriol); from amino alcohols (non-limiting examples of which include 20 aminoethanol, dimethylaminoethanol and diethylaminoethanol and their quaternised derivatives); or from alcohol ethers (non-limiting examples of which include methoxyethanol and ethoxyethanol).

- 25 The amides can be unsubstituted, N-alkyl or N-alkylamino mono-substituted, or N,N-dialkyl, or N,N-dialkylamino disubstituted, wherein the alkyl or alkylamino groups can be derived from C₁₋₄₀ straight chain, C₃₋₄₀ branched chain, or C₃₋₄₀ carbocyclic moieties. In addition, the alkylamino groups 30 can be quaternised, however it is preferred if they are not quaternised.

Also useful as monomers are protected and unprotected acrylic or/and methacrylic acids, salts, esters and amides thereof, wherein the substituents are on the two and three 5 carbon position of the acrylic and/or methacrylic acids, and are independently selected from C₁₋₄ alkyl, hydroxyl, halide (-Cl, -Br, -F, -I), -CN, and -CO₂H, for example methacrylic acid, ethacrylic acid, alpha-chloroacrylic acid and 3-cyano acrylic acid. The salts, esters, and amides of these 10 substituted acrylic and methacrylic acids can be defined as described above for the acrylic/methacrylic acid salts, esters and amides.

Other useful monomers include: vinyl and allyl esters of C₁₋₄₀ 15 straight chain, C₃₋₄₀ branched chain, or C₃₋₄₀ carbocyclic carboxylic acids; vinyl and allyl halides (e.g. vinyl chloride, allyl chloride); pyridines substituted with one or more vinyl or allyl groups (e.g. vinyl pyridine, allyl pyridine); vinylidene chloride; and hydrocarbons having at 20 least one unsaturated carbon-carbon double bond (e.g. styrene, alpha-methylstyrene, t-butylstyrene, butadiene, isoprene, cyclohexadiene, ethylene, propylene, 1-butene, 2-butene, isobutylene, p-methylstyrene); and mixtures thereof.

25 Preferred monomers useful herein include those selected from protected and unprotected acrylic acid, methacrylic acid, ethacrylic acid, methyl acrylate, ethyl acrylate, n-butyl acrylate, -iso-butyl acrylate, -t-butyl acrylate, 2-ethylhexyl acrylate, decyl acrylate, octyl acrylate, methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, iso-butyl methacrylate, t-butyl methacrylate, 2-ethylhexyl

methacrylate, decyl methacrylate, methyl ethacrylate, ethyl ethacrylate, n-butyl ethacrylate, iso-butyl ethacrylate, t-butyl ethacrylate, 2-ethylhexyl ethacrylate, decyl ethacrylate, 2,3-dihydroxypropyl acrylate, 2,3-
5 dihydroxypropyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, hydroxypropyl methacrylate, glycetyl monoacrylate, glycetyl monoethacrylate, glycidyl methacrylate, glycidyl acrylate, acrylamide, methacrylamide, ethacrylamide, N-methyl acrylamide, N,N-dimethyl acrylamide,
10 N,N-dimethyl methacrylamide, N-ethyl acrylamide, N-isopropyl acrylamide, N-butyl acrylamide, N-t-butyl acrylamide, N,N-di-n-butyl acrylamide, N,N-diethylacrylamide, N-octyl acrylamide, N-octadecyl acrylamide, N,N-diethylacrylamide, N-phenyl acrylamide, N-methyl methacrylamide, N-ethyl
15 methacrylamide, N-dodecyl methacrylamide, N,N-dimethylaminoethyl acrylamide, quaternised N,N-dimethylaminoethyl acrylamide, N,N-dimethylaminoethyl methacrylamide, quaternised N,N-dimethylaminoethyl methacrylamide, N,N-dimethylaminoethyl acrylate, N,N-
20 dimethylaminoethyl methacrylate, quaternised N,N-dimethylaminoethyl acrylate, quaternised N,N-dimethylaminoethyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxyethyl ethacrylate, glycetyl acrylate, 2-methoxyethyl acrylate, 2-methoxyethyl methacrylate, 2-
25 methoxyethyl ethacrylate, 2-ethoxyethyl acrylate, 2-ethoxyethyl methacrylate, 2-ethoxyethyl ethacrylate, maleic acid, maleic anhydride and its half esters, fumaric acid, itaconic acid, itaconic anhydride and its half esters, crotonic acid, angelic acid, diallyldimethyl ammonium
30 chloride, vinyl pyrrolidone, vinyl imidazole, methyl vinyl ether, methyl vinyl ketone, maleimide, vinyl pyridine, vinyl

- 12 -

furan, styrene sulphonate, allyl alcohol, allyl citrate, allyl tartrate, vinyl acetate, vinyl alcohol, vinyl caprolactam and mixtures thereof.

- 5 It is particularly preferred that the A groups are polyacrylate blocks or polymethacrylate blocks.

Therefore, more preferred monomers are those selected from methyl acrylate, methyl methacrylate, methyl ethacrylate, 10 ethyl acrylate, ethyl methacrylate, ethyl ethacrylate, n-butyl acrylate, n-butyl methacrylate, n-butyl ethacrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, 2-ethylhexyl ethacrylate, N-octyl acrylamide, 2-methoxyethyl acrylate, 2-hydroxyethyl acrylate, N,N-dimethylaminoethyl acrylate, 15 N,N-dimethylaminoethyl methacrylate, acrylic acid, methacrylic acid, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate and mixtures thereof.

Most preferred monomers are those selected from N,N-dimethylaminoethyl acrylate, N,N-dimethylaminoethyl methacrylate, 2-ethylhexyl acrylate, hydroxyethyl methacrylate, N-octyl acrylamide, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate and mixtures thereof.

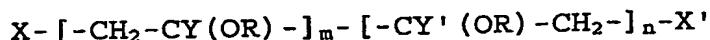
- 25 Even more preferably, the A groups are poly(aminoalkyl methacrylate) blocks, such as, for example, poly(2-(dimethylamino)ethyl methacrylate) blocks.

The B Block

The B block of the polymer is derived from an ethylenically unsaturated carboxylate groups,

5

The B block is preferably represented by the formula:



wherein m and n are integers independently greater than 1; Y 10 and Y' are independently H or -CH₃; R represents a hydrocarbyl group; and X and X' independently represent substituents active for the formation of block polymers in a transition metal mediated, atom transfer polymerisation process.

15

R may be selected from the group consisting of: CH₃C(O)-, Y"-C(O)-, PhC(O)-, Ph-, PhCH₂- CH₃- (CH₂-CH₂-CH₂-CH₂-), 'C(O)-, CH₃- (CH₂-CH=CH-CH₂-) eC(O)- and substituted phenyl; wherein Y" is an n- alkyl group having up to 18 carbon atoms, Ph is phenyl, z' is an integer up to 5000, z" is an integer up to 20 5000 and the substituted phenyl is substituted with at least one substituent selected from the group consisting of NO₂, OMe, CN, NMe₂, OH, CL, Br, and F. Preferably, R is CH₃C(O)-, that is that the b block is derived from vinyl 25 acetate.

The X and X' groups preferably have homolytically cleavable CI and/or Br bonds.

30 Preferably, X and X' are independently selected from the group consisting of BrCH₂C(O)O-; BrC(Me)2C(O)O-..

$\text{BrCH}_2\text{C(O)OCH}_2\text{CH}_2\text{NHC(O)CMe}_2$; and
 $\text{BrCMe}_2\text{C(O)OCH}_2\text{CH}_2\text{NHC(O)CMe}_2$.

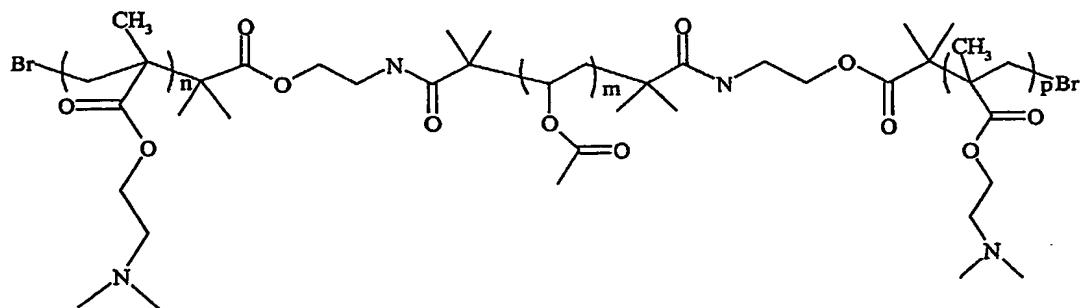
wherein Me represents CH_3 .

- 5 The B block, preferably have a molecular weight M_n in the range of from 100 to 300,000 more preferably from 1,000 to 200,000, most preferably 1,000 to 30,000.

Process for producing ABA block copolymers

10 The polymers of the present invention may be formed by a number of different routes. However, the polymers are preferably formed according to the process described in WO 01/07496 (BP Chemicals Limited)

15 Particularly preferred polymers of the invention are:



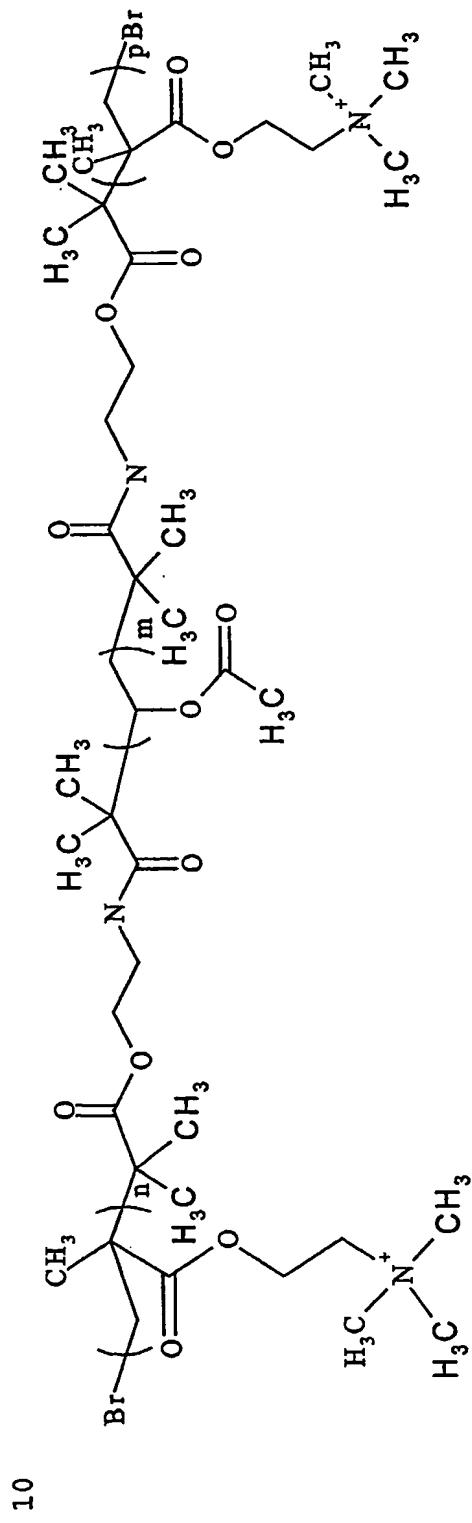
20 DC17: Total M_n = 28 000
 M_n of PVAc = 8 700
 M_n of each block of PDMAEMA = 9 700
 PD = 1.34

25 DC20: Total M_n = 17 400
 M_n of PVAc = 8 700
 M_n of each block of PDMAEMA = 4 350
 PD = 1.45

M_n = Number average molecular weight obtained by Gel Permeation Chromatography using polystyrene standards.

5

PD = Polydispersity



DC 18 = Quaternised DC17

15

DC21 = Quaternised DC20

Compositions of the invention

Cosmetic or personal care compositions of the present
5 invention are preferably formulated into hair care
compositions, especially hairspray compositions, but can
also be formulated into a wide variety of product types,
including mousses, gels, lotions, tonics, sprays, shampoos,
conditioners, rinses, hand and body lotions, facial
10 moisturisers, sunscreens, anti-acne preparations, topical
analgesics, mascaras, and the like. Compositions of the
invention comprise a cosmetically acceptable diluent or
carrier. Preferably, the compositions are for use in
styling human hair and, more preferably, they are packaged
15 and labelled as such.

Compositions of the invention preferably contain the polymer
in an amount of from 0.01% to 30% (more preferably from 0.1
to 10%) by weight. Compositions of the invention may,
20 optionally, comprise a fragrance or perfume and/or one or
more of the optional additional components described
hereinafter.

The carriers and additional components required to formulate
25 such products vary with product type and can be routinely
chosen by one skilled in the art. The following is a
description of some of these carriers and additional
components.

Carriers

Cosmetic or personal care compositions of the present invention can comprise a carrier, or a mixture of such carriers, which are suitable for application to the hair. The carriers are present at from about 0.5% to about 99.5%, preferably from about 5.0% to about 99.5%, more preferably from about 10.0% to about 98.0%, by weight of the composition. As used herein, the phrase "suitable for application to hair" means that the carrier does not damage or negatively affect the aesthetics of hair or cause irritation to the underlying skin.

Carriers suitable for use with hair care compositions of the present invention include, for example, those used in the formulation of hair sprays, mousses, tonics, gels, shampoos, conditioners, and rinses. The choice of appropriate carrier will also depend on the particular polymer to be used, and whether the product formulated is meant to be left on the surface to which it is applied (e.g., hair spray, mousse, tonic, or gel) or rinsed off after use (e.g., shampoo, conditioner, rinse).

The carriers used herein can include a wide range of components conventionally used in hair care compositions. The carriers can contain a solvent to dissolve or disperse the particular polymer being used, with water, the C₁-C₆ alcohols, lower alkyl acetate and mixtures thereof being preferred. The carriers can also contain a wide variety of additional materials such as acetone, hydrocarbons (such as

isobutane, hexane, decene), halogenated hydrocarbons (such as Freons) and volatile silicones such as cyclomethicone.

When the hair care composition is a hair spray, tonic, gel, 5 or mousse the preferred solvents include water, ethanol, volatile silicone derivatives, and mixtures thereof. The solvents used in such mixtures may be miscible or immiscible with each other. Mousses and aerosol hair sprays can also utilise any of the conventional propellants to deliver the 10 material as a foam (in the case of a mousse) or as a fine, uniform spray (in the case of an aerosol hair spray). Examples of suitable propellants include materials such as trichlorofluoromethane, dichlorodifluoromethane, 15 difluoroethane, dimethylether, propane, n-butane or isobutane. A tonic or hair spray product having a low viscosity may also utilise an emulsifying agent. Examples 20 of suitable emulsifying agents include nonionic, cationic, anionic surfactants, or mixtures thereof. If such an emulsifying agent is used, it is preferably present at a level of from about 0.01% to about 7.5% by weight based on 25 total weight of the composition. The level of propellant can be adjusted as desired but is generally from about 3% to about 30% by weight based on total weight for mousse compositions and from about 15% to about 50% by weight based on total weight for aerosol hair spray compositions.

Suitable spray containers are well known in the art and 30 include conventional, non-aerosol-pump-sprays i.e., "atomisers", aerosol containers or cans having a propellant, as described above, and also pump aerosol containers utilising compressed air as the propellant.

Where the hair care compositions are conditioners and rinses, the carrier can include a wide variety of conditioning materials. Where the hair care compositions 5 are shampoos, the carrier can include, for example, surfactants, suspending agents, and thickeners. Hair styling creams or gels also typically contain a structurant or thickener, typically in an amount of from 0.01% to 10% by weight.

10 The carrier can be in a wide variety of forms. For example, emulsion carriers, including oil-in-water, water-in-oil, water-in-oil-in-water, and oil-in-water-in-silicone emulsions, are useful herein. These emulsions can cover a 15 broad range of viscosities, e.g., from about 100 cps to about 200,000 cps. These emulsions can also be delivered in the form of sprays using either mechanical pump containers or pressurised aerosol containers using conventional propellants. These carriers can also be delivered in the 20 form of a mousse. Other suitable topical carriers include anhydrous liquid solvents such as oils, alcohols, and silicones (e.g., mineral oil, ethanol, isopropanol, dimethicone, cyclomethicone, and the like); aqueous-based single phase liquid solvents (e.g., hydro-alcoholic solvent 25 systems); and thickened versions of these anhydrous and aqueous-based single phase solvents (e.g., where the viscosity of the solvent has been increased to form a solid or semi-solid by the addition of appropriate gums, resins, waxes, polymers, salts, and the like).

Additional Components

A wide variety of additional components can be employed in compositions according to the present invention. Examples 5 include the following:

- hair styling polymers for hair styling compositions such as hair sprays, gels, and mousses. Hair styling polymers are well known articles of commerce and many such 10 polymers are available commercially which contain moieties, which render the polymers cationic, anionic, amphoteric or nonionic in nature. The polymers may be synthetic or naturally derived.

15 The amount of the polymer may range from 0.5 to 10%, preferably 0.75 to 6% by weight based on total weight of the composition.

Examples of anionic hair styling polymers are:

20 copolymers of vinyl acetate and crotonic acid;

terpolymers of vinyl acetate, crotonic acid and a vinyl ester of an alpha-branched saturated aliphatic 25 monocarboxylic acid such as vinyl neodecanoate;

copolymers of methyl vinyl ether and maleic anhydride (molar ratio about 1:1) wherein such copolymers are 50% esterified with a saturated alcohol containing from 1 to 4 carbon atoms 30 such as ethanol or butanol;

acrylic copolymers containing acrylic acid or methacrylic acid as the anionic radical-containing moiety with other monomers such as: esters of acrylic or methacrylic acid with one or more saturated alcohols having from 1 to 22 carbon atoms (such as methyl methacrylate, ethyl acrylate, ethyl methacrylate, n-butyl acrylate, t-butyl acrylate, t-butyl methacrylate, n-butyl methacrylate, n-hexyl acrylate, n-octyl acrylate, lauryl methacrylate and behenyl acrylate); glycols having from 1 to 6 carbon atoms (such as hydroxypropyl methacrylate and hydroxyethyl acrylate); styrene; vinyl caprolactam; vinyl acetate; acrylamide; alkyl acrylamides and methacrylamides having 1 to 8 carbon atoms in the alkyl group (such as methacrylamide, t-butyl acrylamide and n-octyl acrylamide); and other compatible unsaturated monomers.

The polymer may also contain grafted silicone, such as polydimethylsiloxane.

Specific examples of suitable anionic hair styling polymers are:

RESYN® 28-2930 available from National Starch (vinyl acetate/crotonic acid/vinyl neodecanoate copolymer);

ULTRAHOLD® 8 available from BASF (CTFA designation Acrylates/acrylamide copolymer);

the GANTREZ®ES series available from ISP corporation esterified copolymers of methyl vinyl ether and maleic anhydride).

Other suitable anionic hair styling polymers include carboxylated polyurethanes. Carboxylated polyurethane resins are linear, hydroxyl-terminated copolymers having 5 pendant carboxyl groups. They may be ethoxylated and/or propoxylated at least at one terminal end. The carboxyl group can be a carboxylic acid group or an ester group, wherein the alkyl moiety of the ester group contains one to three carbon atoms. The carboxylated polyurethane resin can 10 also be a copolymer of polyvinylpyrrolidone and a polyurethane, having a CTFA designation PVP/polycarbamyl polyglycol ester. Suitable carboxylated polyurethane resins are disclosed in EP-A-0619111 and US Patent No. 5,000,955. Other suitable hydrophilic polyurethanes are disclosed in US 15 Patent Nos. 3,822,238; 4,156,066; 4,156,067; 4,255,550; and 4,743,673.

Amphoteric hair styling polymers which can contain cationic groups derived from monomers such as t-butyl aminoethyl 20 methacrylate as well as carboxyl groups derived from monomers such as acrylic acid or methacrylic acid can also be used in the present invention. One specific example of an amphoteric hair styling polymer is Amphomer® (Octylacrylamide/ acrylates/butylaminoethyl methacrylate 25 copolymer) sold by the National Starch and Chemical Corporation.

----- Examples of nonionic hair styling polymers are homopolymers-----
of N-vinylpyrrolidone and copolymers of N-vinylpyrrolidone 30 with compatible nonionic monomers such as vinyl acetate. Nonionic polymers containing N-vinylpyrrolidone in various

weight average molecular weights are available commercially from ISP Corporation - specific examples of such materials are homopolymers of N-vinylpyrrolidone having an average molecular weight of about 630,000 sold under the name PVP K-5 90 and are homopolymers of N-vinylpyrrolidone having an average molecular weight of about 1,000,000 sold under the name of PVP K-120.

Other suitable nonionic hair styling polymers are cross-linked silicone resins or gums. Specific examples include rigid silicone polymers such as those described in EP-A-10 0240350 and cross-linked silicone gums such as those described in WO 96/31188.

Examples of cationic hair styling polymers are copolymers of 15 amino-functional acrylate monomers such as lower alkyl aminoalkyl acrylate, or methacrylate monomers such as dimethylaminoethyl methacrylate, with compatible monomers such as N-vinylpyrrolidone, vinyl caprolactam, alkyl 20 methacrylates (such as methyl methacrylate and ethyl methacrylate) and alkyl acrylates (such as ethyl acrylate and n-butyl acrylate).

Specific examples of suitable cationic polymers are:
25

copolymers of N-vinylpyrrolidone and dimethylaminoethyl methacrylate, available from ISP Corporation as Copolymer 845, Copolymer 937 and Copolymer 958;

copolymers of N-vinylpyrrolidone and dimethylaminopropylacrylamide or methacrylamide, available from ISP Corporation as Styleze® CC10;

5 copolymers of N-vinylpyrrolidone and dimethylaminoethyl methacrylate;

copolymers of vinylcaprolactam, N-vinylpyrrolidone and dimethylaminoethylmethacrylate;

10 Polyquaternium-4 (a copolymer of diallyldimonium chloride and hydroxyethylcellulose);

Polyquaternium-11 (formed by the reaction of diethyl sulphate and a copolymer of vinyl pyrrolidone and dimethyl aminoethylmethacrylate), available from ISP as Gafquat® 734, 15 755 and 755N, and from BASF as Luviquat® PQ11;

Polyquaternium-16 (formed from methylvinylimidazolium chloride and vinylpyrrolidone), available from BASF as 20 Luviquat® FC 370, FC 550, FC 905 and HM-552;

Polyquaternium-46 (prepared by the reaction of vinylcaprolactam and vinylpyrrolidone with 25 methylvinylimidazolium methosulphate), available from BASF as Luviquat® Hold.

Examples of suitable naturally-derived polymers include shellac, alginates, gelatins, pectins, cellulose derivatives 30 and chitosan or salts and derivatives thereof. Commercially

available examples include Kytamer® (ex Amerchol) and Amaze® (ex National Starch).

Also suitable for use as optional components in the
5 compositions of the invention are the ionic copolymers
described in WO 93/03703, the polysiloxane-grafted polymers
disclosed in WO 93/23446, the silicone-containing
polycarboxylic acid copolymers described in WO 95/00106 or
WO 95/32703, the thermoplastic elastomeric copolymers
10 described in WO 95/01383, WO 95/06078, WO 95/06079 and WO
95/01384, the silicone grafted adhesive polymers disclosed
in WO 95/04518 or WO 95/05800, the silicone macro-grafted
copolymers taught in WO 96/21417, the silicone macromers of
WO 96/32918, the adhesive polymers of WO 98/48770 or WO
15 98/48771 or WO 98/48772 or WO 98/48776, the graft polymers
of WO 98/51261 and the grafted copolymers described in WO
98/51755.

With certain of the above-described polymers it may be
20 necessary to neutralise some acidic groups to promote
solubility/dispersibility. Examples of suitable
neutralising agents include 2-amino-2-methyl-1,3-
propanediol (AMPD); 2-amino-2-ethyl-1,3-propanediol (AEPD);
2-amino-2-methyl-1-propanol (AMP); 2-amino-1-butanol (AB);
25 monoethanolamine (MEA); diethanolamine (DEA);
triethanolamine (TEA); monoisopropanolamine (MIPA);
diisopropanol-amine (DIPA); triisopropanolamine (TIPA); and
dimethyl stearamine (DMS). A long chain amine neutralising
agent such as stearamidopropyl dimethylamine or
30 lauramidopropyl dimethylamine may be employed, as is
described in US 4,874,604. Also suitable are inorganic

neutralisers, examples of which include sodium hydroxide, potassium hydroxide and borax. Mixtures of any of the above neutralising agents may be used. Amounts of the neutralising agents will range from about 0.001 to about 10%

5 by weight of the total composition.

- sunscreening agents such as 2-ethylhexyl p-methoxycinnamate, 2-ethylhexyl N,N-dimethyl-p-aminobenzoate, p-aminobenzoic acid, 2-phenylbenzimidazole-5-sulfonic acid, 10 octocrylene, oxybenzone, homomenthyl salicylate, octyl salicylate, 4,4'-methoxy-t-butylidibenzoylmethane, 4-isopropyl dibenzoylmethane, 3-benzylidene camphor, 3-(4-methylbenzylidene) camphor, titanium dioxide, zinc oxide, silica, iron oxide, and mixtures thereof.

15

- anti-dandruff actives such as zinc pyrithione, piroctone olamine, selenium disulphide, sulphur, coal tar, and the like.

20

- hair conditioning agents such as hydrocarbons, silicone fluids, and cationic materials. The hydrocarbons can be either straight or branched chain and can contain from about 10 to about 16, preferably from about 12 to about 16 carbon atoms. Examples of suitable hydrocarbons are decane, 25 dodecane, tetradecane, tridecane, and mixtures thereof.

Examples of suitable silicone conditioning agents useful herein can include either cyclic or linear

... polydimethylsiloxanes, -phenyl- and -alkyl-phenyl-silicones, ... and silicone copolyols. Cationic conditioning agents useful

30 herein can include quaternary ammonium salts or the salts of fatty amines.

- surfactants for hair shampoo and conditioner compositions. For a shampoo, the level is preferably from about 10% to about 30%, preferably from 12% to about 25%, by 5 weight based on total weight of the composition. For conditioners, the preferred level of surfactant is from about 0.2% to about 3%, by weight based on total weight of the composition. Surfactants useful in compositions of the present invention include anionic, nonionic, cationic, 10 zwitterionic and amphoteric surfactants.

- carboxylic acid polymer thickeners for hair shampoo and conditioner compositions. These crosslinked polymers contain one or more monomers derived from acrylic acid, 15 substituted acrylic acids, and salts and esters of these acrylic acids and the substituted acrylic acids, wherein the crosslinking agent contains two or more carbon-carbon double bonds and derived from a polyhydric alcohol. Examples of carboxylic acid polymer thickeners useful herein are those 20 selected from the group consisting of carbomers, acrylates/C10-C30 alkyl acrylate crosspolymers, and mixtures thereof. Compositions of the present invention can comprise from about 0.025% to about 1%, more preferably from about 0.05% to about 0.75% and most preferably from about 0.10% to 25 about 0.50% of the carboxylic acid polymer thickeners, by weight based on total weight of the composition.

- emulsifiers for emulsifying the various carrier components of the compositions of the invention. Suitable 30 emulsifier types include polyethylene glycol 20 sorbitan monolaurate (Polysorbate 20), polyethylene glycol 5 soya

sterol, Steareth-20, Ceteareth-20, PPG-2 methyl glucose ether distearate, Ceteth-10, Polysorbate 80, cetyl phosphate, potassium cetyl phosphate, diethanolamine cetyl phosphate, Polysorbate 60, glyceryl stearate, PEG-100

5 stearate, and mixtures thereof. The emulsifiers can be used individually or as a mixture of two or more and can comprise from about 0.1% to about 10%, more preferably from about 1% to about 7%, and most preferably from about 1% to about 5%, by weight based on total weight of the composition.

10

- vitamins and derivatives thereof (e.g., ascorbic acid, vitamin E, tocopheryl acetate, retinoic acid, retinol, retinoids, and the like).

15

- cationic polymers (e.g., cationic guar gum derivatives such as guar hydroxypropyltrimonium chloride and hydroxypropyl guar hydroxypropyltrimonium chloride, available as the Jaguar® series from Rhone-Poulenc).

20

- preservatives, antioxidants, chelators and sequestrants; and aesthetic components such as fragrances, colourings, hair nutrients and essential oils.

25

The invention also involves a method of styling hair by applying thereto a styling composition as is hereinabove described.

30

-- -- -- The following non-limiting Examples further illustrate the preferred embodiments of the invention. All percentages referred to are by weight based on total weight unless otherwise indicated.

EXAMPLESBond strength analysis

5

1 μ l of the 3% solids formulations were prepared using the ABA block copolymers of the invention (as described above as preferred materials) pipetted onto a hair junction. The following bond strengths were obtained.

10

Diastron MTT600 parameters: % extension =100
Rate (mm/min) =10
Max force(g) = 200
Gauge force(gmf) = 2

15

Temperature = 25°C

20

	Ave Bond Strength (g) at 60% RH	Ave Bond Strength (g) at 80% RH
DC17	36.6+/- 7.0	28.0+/-4.0
DC18	10.2+/- 3.3	5.4+/-2.2
DC20	38.7+/-5.8	32.9+/- 4.1
DC21	8.0+/- 3.1	8.6+/-2.3

The non-quaternised version of the polymer gave superior bond strength data than the quaternised version.

25

- 30 -

Examples 1,2 and Comparative Example A

The following pump spray compositions were prepared:

	Example 1	Example 2	Example A
Polymer DC17	3		
Polymer DC20		3	
SCJ polymer			3
ethanol	55	55	55
water	42	42	42

5

Polymer DC17 and polymer DC20 as described above.

SCJ polymer is a commercially available styling polymer - poly (ethyl-methacrylate-co-methacrylic acid-co-
10 butylacrylate)

The compositions were tested by washing a wig twice with commercially available shampoo. The wig's hair is placed in velcro rollers and dried under a hood dryer for 20 minutes
15 to set the style. The rollers are carefully removed and the initial style photographed. A shield was placed over over half of the wig and the remaining half was treated with the Example by pumping the composition from a pump spray for 6 pumps. The shield was placed over the treated side of the
20 wig and the second half of the wig was treated with a second Example in an identical manner. Photographs are taken throughout the study. The style retention is monitored by the stylist over a 30 minute time period under a controlled environment using the Sanyo Gallenkamp Chamber.

Conditions 21-22°C/34-35 % Humidity

<u>Attribute</u>	<u>Treated</u>	
	<u>Head A</u>	<u>Head B</u>
	<u>Example 2</u>	<u>Example A</u>
Hold	3	9
Softest	12	0
Stickiest	2	10
Deposits	2	10
Flexible	10	2
Natural Movement	12	0

5

10 Conditions 25-27°C/41-46% Humidity

<u>Attribute</u>	<u>Treated</u>	
	<u>Head A</u>	<u>Head B</u>
	<u>Example 1</u>	<u>Example A</u>
Hold	6	6
Softest	10	2
Stickiest	7	5
Deposits	3	9
Flexible	9	3
Natural Movement	9	3

15

Examples 3 to 8

The following are examples of compositions according to the
5 invention.

The materials used in the examples include the following:

	<u>Material</u>	<u>Supplier</u>	<u>Function</u>
10	Silicone emulsion X2 1787 TM	Dow Corning	conditioning
	VOLPO CS 50 TM	Croda Chemicals	surfactant
	Sepicide LD TM	Seppic	preservative
	Cremophor RH410 TM	BASF	stabiliser
	Silicone DC 200/DC 24 S TM	Dow Corning	conditioning
15	Silwet L7602/L-720 TM	Union Carbide	surfactant
	CAP 40 TM	Calor Gas	propellant
	Carbopol 980 TM	BF Goodrich	structurant
	Jaguar HP-105 TM	Rhodia	conditioning
	Silicone Fluid 245 TM	Dow Corning	conditioning
20	Ethanol is SD Alcohol 40-B (92% active)		

Example 3

A styling mousse is formulated as follows:

Material	% in product (w/w)
Silicone Emulsion X2 1787	1.2
Polymer of any of Examples 1 to 2	1.5
VOLPO CS 50	0.3
Sepicide LD	0.4
Cremophor RH410	0.2
Ethanol	7.5
CAP 40	8.0
Perfume	0.2
Water	to 100%

5

Example 4

A hairspray is formulated as follows:

Material	% in product (w/w)
Polymer of any of Examples 1 to 2	3.0
Silicone DC200	0.09
Silwet L7602	0.09
CAP 40	35.0
Ethanol	60.0
Perfume	0.10
Water	to 100%

10

Example 5

5 A pump spray is formulated as follows:

Material	% w/w
Ethanol	60.0
Polymer of any of Examples 1 to 2	3.5
Silwet L-720	0.3
Silicone DC24S	0.15
Fragrance	0.3
Water	to 100%

Example 6

10 A styling gel is formulated as follows:

Material	% w/w
Polymer of any of Examples 1 to 2	3.8
Carbopol 980	0.4
Water	to 100%
Sepicide LD	0.4
Sodium hydroxide (8% 2M)	0.1
Ethanol	10.0
Cremaphor RH410	0.4
Jaguar HP-105	0.2
Perfume	0.15

Example 7

5 A 55% voc propelled aerosol composition is formulated as follows:

Material	% w/w
Polymer of any of Examples 1 to 2	3.75
Silicone Fluid 245	0.20
Fragrance	0.32
Ethanol	19.53
Dimethyl ether	35.00
Sodium benzoate	0.26
Cyclohexylamine	0.21
Water	to 100%

Example 8

A 55% voc pump hairspray composition is formulated as follows:

5

Material	% w/w
Polymer of any of Examples 1 to 2	3.75
Cyclopentasiloxane (99% active)	0.15
Benzophenone 4	0.0001
Fragrance	0.25
Ethanol	58.00
Water	to 100%

10

15

20

CLAIMS

1. A personal care composition comprising
 - i) a polymer comprising an ABA block copolymer,wherein the A groups are polymeric blocks built up from an ethylenically unsaturated polymerisable monomer and the B group is derived from an ethylenically unsaturated carboxylate and,
 - ii) a cosmetically acceptable diluent or carrier.
- 10 2. A personal care composition as claimed in Claim 1 wherein the A groups of the polymer are derived from acrylate blocks or methacrylate blocks.
- 15 3. A personal care composition as claimed in Claim 2, wherein the A groups of the polymer are poly(aminoalkyl methacrylate) blocks.
4. A personal care composition as claimed in Claim 3, wherein the A groups of the polymer are poly(2-(dimethylamino)ethyl methacrylate) blocks.
- 20 5. A personal care composition according to any preceding claim wherein the B group of the polymer is derived from vinylacetate.
- 25 6. A personal care composition according to any preceding claim in which the molecular weight M_n of the total polymer is from 5,000 to 500,000.

7. A personal care composition according to any preceding claim in which the molecular weight M_n of each A block of the polymer is from 1,000 to 100,000.
- 5 8. A personal care composition according to any preceding claim in which the molecular weight M_n of each B block of the polymer is from 1,000 to 200,000
9. A personal care composition as claimed in any one of 10 the preceding claims wherein the polymer is soluble in a solvent selected from water, ethanol and mixtures thereof.
10. A personal care composition as claimed in any preceding 15 claim, further comprising a fragrance or perfume.
11. Composition as claimed in any preceding claim which is a hair styling composition.
- 20 12. Composition as claimed in any preceding claim which comprises from 0.1 to 10% by weight of the polymer.
13. Composition as claimed in any preceding claim further comprising an additional hair styling polymer.
- 25 14. Composition as claimed in any preceding claim, further comprising from 0.01% to 7.5% by weight of a surfactant.
- 30 15. Composition as claimed in any preceding claim, further comprising up to 30% by weight of a propellant.

16. Composition as claimed in any preceding claim which is a hair styling cream or gel including from 0.01% to 10% by weight of a structurant or thickener.

5

17. A cosmetic method of treating hair which comprises applying to the hair a composition according to any preceding claim.

10 18. Use of a composition according to any one of Claims 1 to 16 for the cosmetic treatment of hair.

ABSTRACT

5

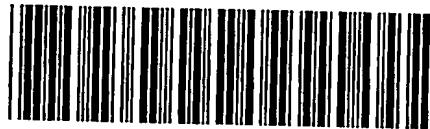
A personal care composition comprising

- 10
- ii) a polymer comprising an ABA block copolymer, wherein the A groups are polymeric blocks built up from an ethylenically unsaturated polymerisable monomer and the B group is derived from an ethylenically unsaturated carboxylate and,
 - ii) a cosmetically acceptable diluent or carrier.

30/770 (1977-07-01)

1977-07-01

PCT/EP2004/002852



This Page is inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT OR DRAWING
- BLURED OR ILLEGIBLE TEXT OR DRAWING
- SKEWED/SLANTED IMAGES
- COLORED OR BLACK AND WHITE PHOTOGRAPHS
- GRAY SCALE DOCUMENTS
- LINES OR MARKS ON ORIGINAL DOCUMENT
- REPERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.
As rescanning documents *will not* correct images problems checked, please do not report the problems to the IFW Image Problem Mailbox